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Third Quarterly Report
for
Solar Cell Contact Development

Contract No.: NAS 5-11595

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for
Goddard Space Flight Center
Greenbelt, Maryland

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(28 Dec. 1968 - 28 March 1969)

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SUMMARY

This report describes the technical work performed during the third quarter of a 12 month research contract, No. NAS 5-11595, for NASA-Goddard Space Flight Center. The contract objectives are twofold: (1) to identify the Ti-Ag contact degradation mechanism on Si solar cells and (2) to determine whether sputter deposition of contact material is compatible with present solar cell configurations.

Contract work during the third quarter involved both the study of contact degradation and sputter deposition of contact material. Exposure of Ti-Ag contacts to an additional number of gaseous environments demonstrated the general porosity of thin Ag films to corrosive species and indicated the extent of the corrosion reaction. The environments included vapors of HCl, HF, H₂SO₄, wet and dry CO₂, and wet and dry Cl₂. Titanium metal was found to be reactive to some of these gases, to seawater, and to ordinary tap water. The corrosion reaction of Ti in aqueous NaOH was found to be concentration dependent, while the reaction rate was not found to be substantially different when Ti was coupled to Ag in solution. A sputtering system was assembled in which Ti and Ag can be sequentially sputtered in situ and where the sputtering targets can be precleaned prior to contact deposition. Deposition of Ti-Ag contacts by sputtering is in progress.

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SECTION I

Introduction

The Ti-Ag contacts currently employed on the solderless type Si solar cells are known to degrade in storage. High relative humidity at a somewhat elevated temperature often accelerates the degradation process.¹ Advanced stages of degradation reveal blisters on the contact and at times the contact peels from the solar cell. Contact peeling has been found to be enhanced by fabrication induced and thermal stresses exerted by solar cell interconnections. The net result of contact degradation is the loss in power efficiency of individual solar cells or of an array of solar cells as found on solar cell panels.

One objective of this contract is to identify the cause of Ti-Ag contact degradation and to recommend to the industry guidelines for fabricating non-degrading contacts. A second objective is to determine whether sputter deposition of contact material is compatible with present solar cell configurations.

Our approach to the first objective has been manifold and included optical inspection of degraded contacts, electron microprobe and Auger Electron Spectroscopy analysis of contacts, electron mirror microscopy (EMM) inspection, potential probe measurements, chemical reactivity studies of Ti and Ag, and others. The overall results of past work have indicated that the degradation process is basically a corrosion phenomena in which corrosive species are capable of penetrating through the overlayer film of Ag and chemically and/or electro-chemically reacting with the underlying layer of Ti.

One of the objectives of more recent studies has been to evaluate the porosity of Ag films to an additional number of potentially corrosive environments. Porosity has been deduced by noting the appearance of blisters on Ti-Ag contacts. Concentrated solutions of NaCl, NaOH, and KOH have been reported effective in producing blisters in addition to high humidity-temperature environments. During this quarter additional corrosive environments were found to cause blistering and are reported herein.

Corrosion processes can be broadly classified into two categories, namely, pure chemical corrosion and galvanic corrosion. The former is sometimes referred to as "dry" corrosion and the latter "wet" corrosion. Additional experiments were performed this quarter with the purpose of defining the role these two corrosion mechanisms play in the degradation of Ti-Ag contacts. It should be noted that Telefunken Laboratories has already suggested that contact degradation proceeds by galvanic corrosion in which the Ag and Ti form a galvanic couple.

SECTION II

Technical Discussion

A. Contact Degradation Studies

1. Exposure of Ti-Ag Contacts to Corrosive Environments

If Ti-Ag contact degradation is the result of direct chemical or electrochemical attack of the Ti layer as we believe, then thin films of Ag, as found on these contacts, must be porous to corrosive environments. Data presented in the Second Quarterly Report tend to substantiate the porosity of Ag films. Electrolytes of NaCl, NaOH, and KOH were reported to blister Ti-Ag contacts in a relatively short period of time. This quarter additional studies were conducted for the purpose of evaluating the porosity of Ag films to other corrosive environments. Ti-Ag contacts were exposed to vapors of HF, HCl, H₂SO₄, wet and dry CO₂, and wet and dry Cl₂.

Vapors of HF, HCl, and H₂SO₄ were obtained by placing a small amount of their concentrated acid solutions in separate glass beakers and the Ti-Ag contacts were mounted on glass pedestals out of solution. The beakers were covered to concentrate the fumes.

Vapors from 48% HF were found to readily degrade a Ti-Ag contact as observed by the development of blisters and wrinkling of the contact in several hours. This result is perhaps not too surprising because HF acid is known to readily attack Ti. It does show, however, that the Ag film (a thickness of 1 μ used here) did not provide sufficient protection for the Ti. Subsequently it was possible to strip the Ag film from the Si wafer with ease. The exposed interface showed signs of discoloration. A polycrystalline strip of Ti was also exposed to HF vapors at the same time and a thick, black film developed on the Ti.

Vapors from 37% HCl also caused severe blistering of a Ti-Ag contact. The size of the blisters was much smaller than found in HF but was typical of those found on degraded solar cells. Some discoloration of the Ag film was noted and a marked reduction in adhesion occurred as in HF above. A thin, dark film developed on the Ti sample.

Vapors from 60% H_2SO_4 gave altogether different results. The Ag film became light to dark brown in color and no blisters developed. Adhesion was not impaired. Subsequent scraping of the contact with a sharp instrument removed the tarnished layer and revealed Ag. The Ti sample was also attacked by the vapor which produced a green deposit. These results can be explained by the fact that Ag is reactive to these vapors and forms a tarnished film of probably Ag_2S . The underlying layer of Ti is very likely protected in this case and thus blisters and loss of adhesion are not observed.

Tests in CO_2 and Cl_2 gas were conducted in high pressure stainless steel vessels which could be evacuated prior to admitting these gases. Both dry and wet gas runs were made. Solar cells and samples with unsintered Ti-Ag contacts to Si wafers, similar to those described in the Second Quarterly Report, were placed in the reaction vessels. The latter samples had an Ag film 1μ thick and had a much smoother surface. These samples provided a more sensitive indicator of blistering than the solar cells.

Dry and wet CO_2 exposures were conducted at 800 psi for 18 hr. No visible degradation was noted in the case of dry CO_2 . Wet CO_2 caused buckling and crazing of the Ti-Ag contact on the Si wafer sample and a few blisters developed. The solar cell, on the other hand, did not show any noticeable sign of degradation.

Dry and wet Cl_2 exposures were conducted at 90 psi for 66 hr. Both environments produced considerable changes in the physical appearance of Ti-Ag contacts. Dry Cl_2 discolored the Ag and profuse colors were noted on the interface exposed by peeling the Ag layer. Wet Cl_2 converted the entire contact to a soft wax-like substance which could be easily removed by scraping. No blisters were evident in either case.

2. Reactivity of Ti in Various Electrolytes

Bulk samples of Ti were immersed in room temperature solutions of 2.0, 0.2, and 0.02 N NaOH, 80° to 90° C ordinary tap water, seawater, and distilled water for the purpose of noting if surface films develop in these environments. The reactivity of Ti was found to be strongly dependent on the concentration of NaOH solution as noted by the time required to develop a surface film. The 2.0 N solution developed a visible film in several hours whereas the 0.2 N

solution developed a film in several days. The 0.02 N solution did not produce a visible film during the 10 days of these tests.

Ordinary tap water and seawater at 80° to 90° C were also very effective in producing a visible film on Ti. Hot distilled water, on the other hand, produced only a faintly visible film.

3. Galvanic vs. Pure Chemical Corrosion of Ti

A limited amount of effort was directed at distinguishing galvanic corrosion from pure chemical corrosion of Ti. We have seen that a passivating-type surface film forms on Ti when placed in solutions of NaOH, KOH, tap water, and seawater without the use of a second electrode such as Ag. If galvanic corrosion is active in the degradation of Ti-Ag contacts, it should be possible to observe a difference in the growth rate of the surface film when Ti is coupled to an Ag electrode in solution. A 1 N solution of NaOH was prepared and reactivity of Ti was recorded by weight change measurements under coupled and uncoupled conditions. Within the experimental accuracy of these measurements, the weight gain of the two Ti electrodes were the same in these two cases as shown in Figure 1. 20 mil sheets of Ti measuring 7 x 8 cm and weighing approximately 7 g were used in these experiments.

These results appear to rule out galvanic corrosion by the couple action. There were, however, several observations which indicated that the couple was active to some extent. First, a galvanic current was found to flow between the couple when short-circuited and an open voltage of ~0.8V was observed. Second, gas (probably hydrogen) was found to be liberated at the Ag electrode under short-circuit conditions. And lastly, a visibly thicker film developed locally on Ti when the Ag electrode was placed close to or in direct contact with the Ti electrode.

Galvanic corrosion may also occur by local action, i.e., both cathodic and anodic regions may exist on Ti due to impurities in Ti, variations in crystallite orientations, local stresses, or possibly other non-homogeneities in Ti. We believe that the formation of the surface film observed here in NaOH is principally by local action. A clarification of the role of the Ti-Ag couple on corrosion when the two metals are placed in intimate contact requires further study.

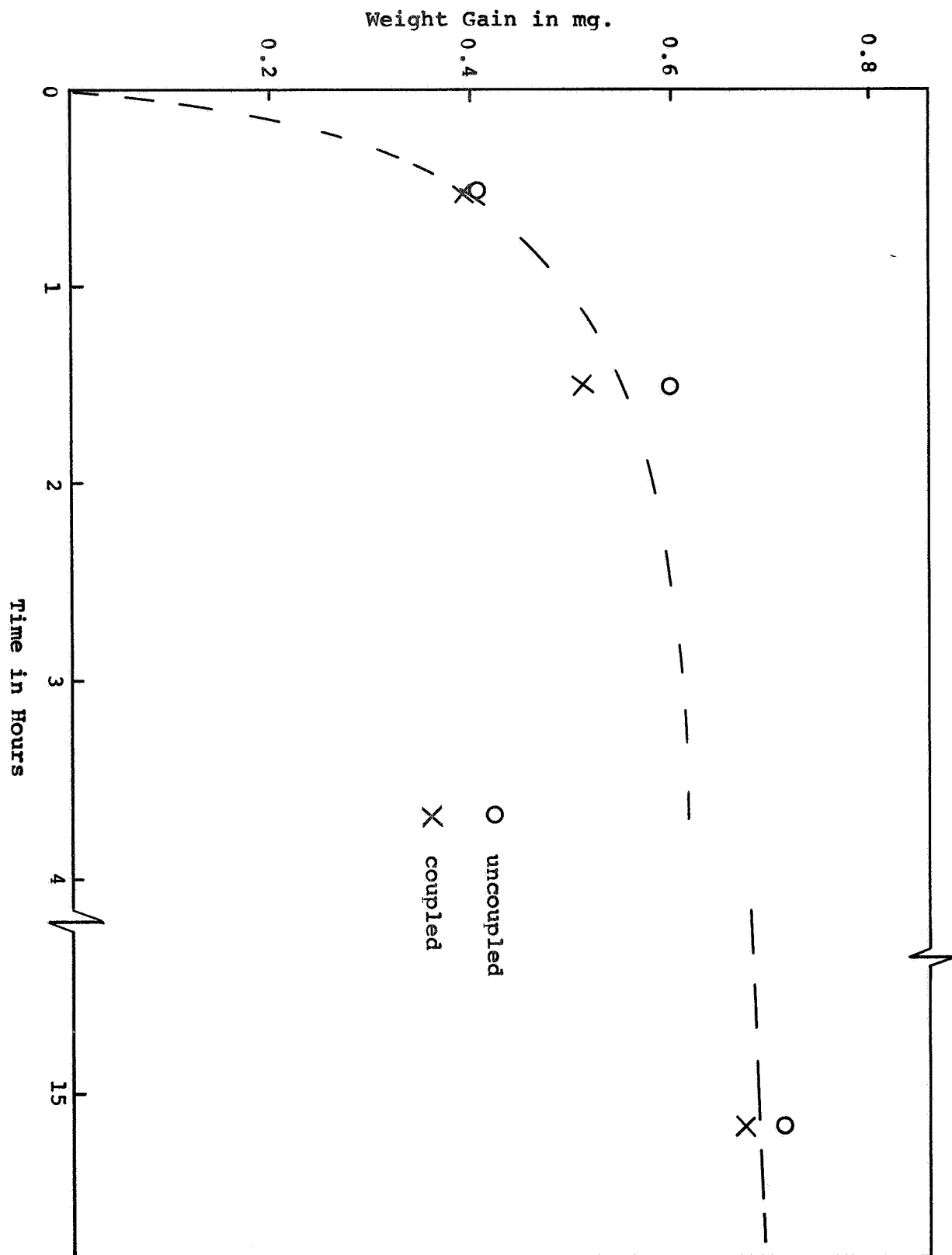


Figure 1 Weight gain of Ti as a function of time of immersion in a 1 N solution of NaOH when coupled and when not coupled to an Ag electrode

4. Electron Microprobe Analysis

Additional electron microprobe analysis was performed on three degraded solar cells for the specific purpose of identifying possible contaminants in Ti-Ag contacts. Two of the cells had their contacts intact and they were stripped from the cell just prior to analysis. The microprobe was incapable of analyzing elements hydrogen, helium, lithium, boron, nitrogen, and oxygen.

No foreign constituents were detected by our Materials Analysis Corporation (MAC)-400 electron microprobe for the cells analyzed. The two stripped cells exhibited varying amounts of Ti and Ag on the cell/contact interfaces, as observed earlier and reported in the First Quarterly Report, whereas no Ag was detected on the interface of the third RAE cell* which exhibited extensive contact peeling. The level of detection varies among the elements and therefore it is difficult to place an upper limit on the amount of foreign material actually present. Most of the elements should have been detected if their concentration exceeded 1% of the sampling volume. Unfortunately the lighter elements such as nitrogen and oxygen are difficult to detect even when present in large quantities; therefore it was futile to look for them here.

B. Contact Deposition by Sputtering

A major portion of the time was expended on the design and construction of a versatile sputtering system in which Ti and Ag can be sequentially sputtered. Provisions were made for cooling the substrates (solar cells) and for pre-cleaning the targets.

The design of the sputtering system is shown in Figure 2. It is a dc triode sputtering apparatus which incorporates a hot cathode as a source of electrons, an anode to collect electrons, a target, and a substrate holder. The electrons, in going from the cathode to the anode, ionize the Ar gas and thereby create a plasma in the space between the target and the substrate. Sputtering of a target occurs when it is biased negative with respect to plasma potential.

*A defective cell removed from a Radio Astronomy Explorer satellite flight paddle after vacuum flight qualification tests.

The Ti and Ag targets are mounted on opposite sides of a quartz plate. The plate is attached to a 1/2 in. stainless steel rod that protrudes through the upper plate. A double O-ring seal provides a vacuum seal and also allows rotation of the target so that initially Ti and subsequently Ag can face the substrate holder during the sputtering run. A shutter is positioned in front of the substrate holder and can be raised to expose the substrates to sputtered atoms. A second rotatable rod and pulley system is used to activate the shutter. The purpose of the shutter is to protect the substrates while the targets are given a sputter cleaning treatment prior to contact deposition.

The substrate holder is a 3-1/2 in. x 4 in. x 1/4 in. thick copper block that has a cooling coil brazed to the back face. The cooling coil is 1/4 in. copper tubing that passes through the bottom plate and is attached to a water line.

The design of the sputtering system is such that the plasma is almost entirely confined to the space between the target assembly and the substrate holder. This was accomplished by placing a glass sleeve and constricting plate in the pumping port and by positioning the anode above the target and substrate holder. A magnetic field generated by coils mounted exterior to the vacuum system also helps to confine the plasma in the desired region. The magnetic field also serves to enhance the uniformity and increase the density of the plasma.

Several sputtering runs have been made to establish the sputtering rates of Ti and Ag. Typical sputtering rates are 40 Å/min for Ti and 400 Å/min for Ag. Procedures for cleaning the targets and for sputtering the Ti and Ag sequentially have also been established. Sputtering of Ti-Ag contacts to Si wafers is in progress for the purpose of evaluating the physical and electric characteristics of sputtered contacts. Of particular interest is the adhesion and contact resistance of these contacts and how they depend on the various sputtering parameters.

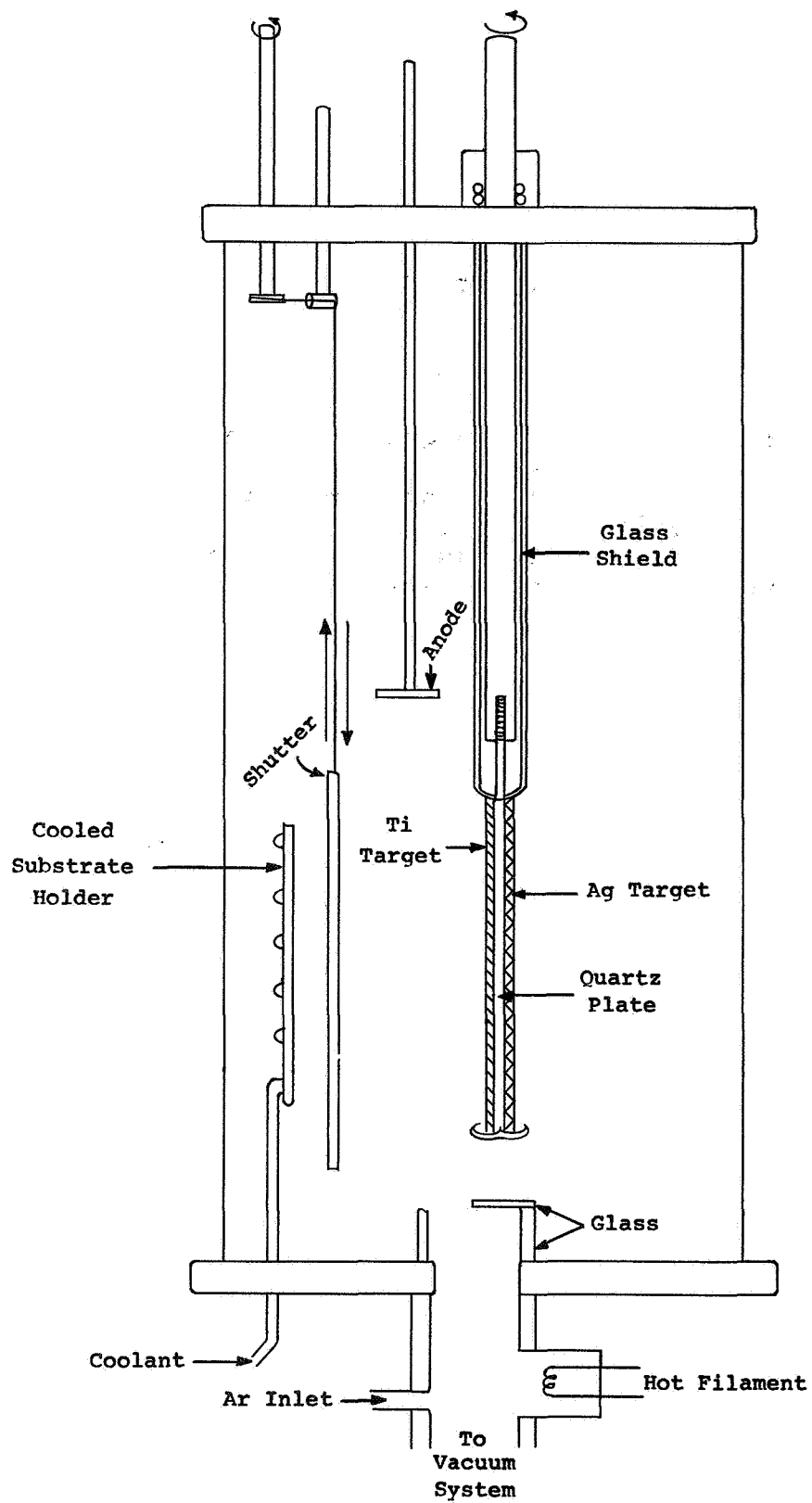


Figure 2 A schematic of the sputtering system.

SECTION III

New Technology

A sputtering system was designed and constructed for the sequential sputter deposition of Ti and Ag. Provisions were made for precleaning the Ti and Ag targets and the substrates by sputtering prior to deposition of contact material. A substrate holder was also incorporated in this system which permits cooling or heating of the substrates during contact deposition.

SECTION IV

Program for the Next Reporting Period

The program for the Fourth Quarter of Contract NAS 5-11595 will include the following:

- 1) Sputter deposition of Ti-Ag contacts onto n- and p-type Si wafers under various controlled deposition conditions.
- 2) Evaluation of sputtered Ti-Ag contacts including adhesion and contact resistance properties.
- 3) Prepare 40 solar cells for delivery to NASA-Goddard Space Flight Center for their evaluation.
- 4) Perform a few selected experiments on the degradation study of solar cell contacts.

SECTION V

Conclusions

The room temperature porosity of thin Ag films such as those employed on Si solar cells has been further substantiated this quarter by noting that vapors from HCl, HF, and wet CO₂ cause blistering of Ti-Ag contacts at ambient temperatures. Corrosive vapors of H₂SO₄ and wet and dry Cl₂ severely attack the Ag film but do not produce blisters.

Of the degrading-type environments studied to date, most are effective in producing visible surface films on Ti. These environments almost always contain water or water vapor and in those cases where water was excluded (dry Cl₂ and CO₂) the reaction was less severe (dry Cl₂) or not apparent at all (dry CO₂). The sensitivity of the corrosion reactions to water content suggests that "wet" or galvanic corrosion is active. Coupling of an Ag electrode to Ti in a 1N solution of NaOH did not enhance the formation of the surface film on Ti when the Ag-to-Ti spacing was several centimeters. The effect of the Ti-Ag couple was, however, evident when the Ag electrode was placed close to or in direct contact with the Ti electrode. These results may be interpreted by assuming that two competing galvanic processes are active--local action and Ti-Ag couple action. Local action is believed to be predominant in the former case and only when the Ti-to-Ag spacing is small does the couple action become apparent. The relative role that these two galvanic processes play in Ti-Ag contacts is not known at this time.

A triode sputtering system was assembled and we are presently sputter depositing Ti-Ag contacts to Si. The physical and electrical properties of these contacts will be evaluated in order to obtain optimum deposition conditions.

LIST OF REFERENCES

- 1 "Temperature and Humidity Effects on Si Solar Cell",
W. Luft, et al, Seventh Photovoltaic Specialist Conference
Proceedings, Pasadena, California, November 1968.